

Negative Ion Mass Spectra of Some Polychlorinated 2-Phenoxyphenols

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Polychlorinated 2-phenoxyphenols were studied by negative ion mass spectrometry. Common to almost all of the methane enhanced negative ion mass spectra were $(M-1)^-$, $(M-36)^{-\bullet}$, $(M-37)^-$, $(M-72)^{-\bullet}$, and chlorinated quinoxide ions. The $(M-36)^{-\bullet}$ ion does not apparently form in a mechanism analogous to the thermal or photochemical ring closure of these compounds to form the chlorinated dioxins. The chlorinated quinoxide ion reflects the number of chlorines on the ring with hydroxy substituent. Collision-induced dissociation mass-analyzed ion kinetic energy spectra (CID-MIKES) from different isomers were qualitatively different in both the normal and charge reversed mode of operation. Comparison of these spectra with those from other classes of polychlorinated aromatic hydrocarbons such as the dioxins or the furans may reveal a common negative ion gas phase chemistry.

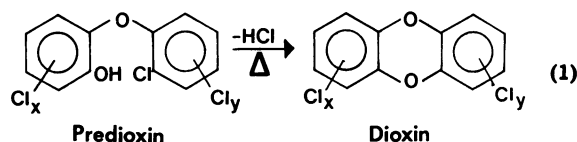
Introduction

Polychlorinated 2-hydroxydiphenyl ethers (also termed polychlorinated 2-phenoxyphenols) were studied by methane-enhanced negative ion mass spectrometry and collision-induced dissociation mass-analyzed ion kinetic energy spectrometry (CID-MIKES). The structures of the compounds studied are shown as I-XII in Figure 1.

The lower chlorinated phenoxyphenols have been used in commercial preparations as bactericides. In addition, those compounds with four to nine chlorines have been shown to be present in technical chlorophenol preparations at levels of from 1 to 5% (1-3). Since the annual production of pentachlorophenol in the United States is about 40000 tons (4), the potential exists for the entry

of 400 tons of chlorinated phenoxyphenols into the environment each year.

The environmental effects of chlorinated phenoxyphenols may be cause for concern, as certain of these compounds may be as toxic as the polychlorinated dioxins or furans (5). In addition, 2-phenoxyphenols have been shown (6-8) to undergo thermal and photochemical ring closure to form dioxins as shown in Eq. (1). Thus, municipal



incineration of refuse is an egregious method for the introduction of both the 2-phenoxyphenols and possibly the dioxins into the environment (9, 10). The yield for conversion to dioxins by thermal ring closure depends on temperature, but can range up to about 5% (11). The yield for photochemical ring closure to form dioxins is about 0.5% (11). Experiments have also shown that chlorophenol preparations themselves may form phenoxyphenols photochemically (12), which may then react further to form the dioxins.

Concern about dioxins, therefore, should be ex-

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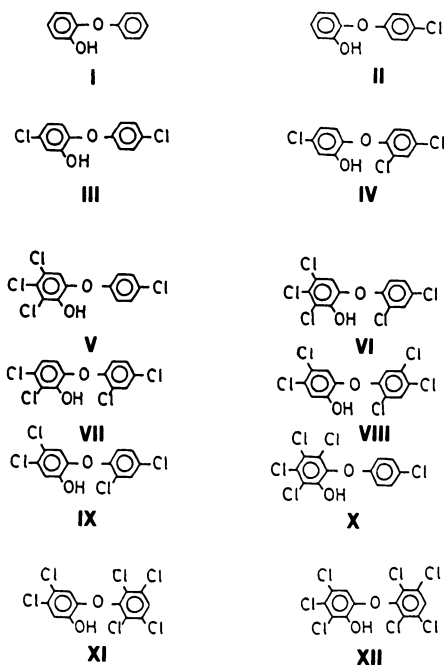


FIGURE 1. Compounds studied.

panded to include the 2-phenoxyphenols. The investigation of these compounds was a logical extension of our negative ion mass spectrometric studies of dioxins (13). Since the first presentation of this data, additional sample compounds have been received and sophisticated MIKES computer software has been developed, so this report should be considered preliminary.

Experimental

Methane-Enhanced Negative Ions

Modifications to a Finnigan quadrupole mass spectrometer to produce negative ions have been described previously (14). Detection of negative ions involved the multiplier described by Stafford (15) in which a Galileo electron multiplier (model 4770) was modified by addition of a copper oxide coated collision surface near the first dynode. To detect positive ions, this surface is held at 0 V and positive ions follow the usual path to the negatively charged first dynode of the electron multiplier. To detect negative ions, +2000 V is imposed upon the surface to attract negative ions, which on collision form positive ions then detected in the normal manner.

Methane-enhanced negative ion spectra were obtained on a Finnigan 3300 quadrupole interfaced directly to a Finnigan 9500 gas chromatograph. Methane (Linde, ultra high purity) was

used as a carrier and moderator gas and the source pressure was 1-2 torr.

The 1.5 m long GC column was packed with 3% OV 17 on 100/200 Gas-Chrom Q, and was temperature-programmed to elute the phenoxyphenol into the ion source within 3 min of injection. Spectra were obtained with source conditions as identical as possible. The source temperature was held constant at 160°C.

CID-MIKES

A VG Micromass ZAB-2F mass spectrometer equipped with a collision cell and MIKES scan unit was used to obtain MIKE spectra. The ion source was operated at 100-200°C with Linde 99.97% methane admitted to give a reading of 8×10^{-5} torr on the source ionization gauge, which corresponds to ca. 0.3 torr in the source. The emission current was 1 mA and the electron energy was 150 eV. Samples were introduced by direct probe. For collision-induced fragmentation, the collision cell was operated at an analyzer ionization gauge reading of $6-8 \times 10^{-7}$ torr. The actual cell pressure then ca. 10^{-3} torr, and the main beam intensity was reduced to ca. 50% of its initial value. Helium was used as collision gas. The MIKE spectra were scanned at 10 msec/eV.

The synthesis of the compounds used in this study has been described elsewhere (11).

Results and Discussion

Methane-Enhanced Negative Ion Mass Spectra

The monoisotopic methane enhanced negative ion mass spectra of twelve phenoxyphenols, with from 0 to 8 chlorines, are summarized in Table 1. Negative ions common to almost all spectra are $(M-1)^-$, $(M-36)^{-}$, $(M-37)^-$, $(M-72)^{-}$, and the chlorinated quinoxide ion.

The $(M-1)^-$ ion is presumably formed by loss of the hydroxyl hydrogen. It should be noted that this $(M-1)^-$ ion does not necessarily form in a method analogous to similar ions formed by negative chemical ionization with OH^- as a reagent ion in which the concentration of OH^- is much higher than that of the sample (16). While the hydroxide ion is ubiquitous contaminant of the background, the sample concentration during peak elution is many times that of this background ion. Consequently, $(M-1)^-$ ion is most likely the result of dissociative resonance capture.

The $(M-36)^{-}$ ion appears in the great majority of these negative ion spectra. In view of the

Table 1. Monoisotopic methane-enhanced negative ion mass spectra of some polychloro-2-phenoxy phenols.

Substitution pattern	Relative abundances					
	(M - 1) ⁻	(M - 36) ⁻	(M - 37) ⁻	(M - 72) ⁻	Quinoxide ^a	Others ^b
---	100	—	—	—	—	—
4'	100	—	—	—	55	(m + 35), 40
4,4'	30	65	—	—	100 (1)	
4,2',4'	—	75	65	100	10 (1)	
3,4,5,4'	100	60	15	—	5 (3)	
3,4,2',4'	100	85	60	65	20 (2)	
4,5,2',4'	100	65	45	80	5 (6)	
3,4,5,2',4'	50	100	100	40	10 (3)	
4,5,2',4',5'	45	45	30	100	40 (2)	
3,4,5,6,4'	85	100	35	15	—	DiClqu, 5 TriClph, 5 TetraClph, 10 TriClph, 25 TetraClph, 10 TriClph, 20 TetraClph, 90
4,5,2',3',5',6'	35	25	—	100	25 (2)	
3,4,5,2',3',5',6'	100	25	—	95	50 (3)	

^a Numbers in parentheses denote number of chlorines.

^b qu = quinoxide; ph = phenoxide.

ring closure mechanism to form dioxins, it might be expected that the formation of this ion might be facilitated from 2-phenoxyphenols with appropriately situated chlorines on the opposite ring. Such an effect is not observed, as seen in Table 1. The formation of (M - 36)⁻ probably occurs by a number of different pathways, as suggested for the polychlorinated diphenyl ethers (17).

Formation of the (M - 37)⁻ ion occurs in two steps, either (M-H₂-Cl)⁻ or (M-H-HCl)⁻ (the former is preferred thermodynamically). The intermediate is not observed. The abundance of this ion will reflect the rates of both steps in its formation, and cannot be expected to yield much structural information. Much the same can be said about the relative abundances of the (M - 72)⁻ ion.

Formation of the quinoxide ion occurs for every chlorinated phenoxyphenol except the 3,4,5,6,4'-isomer and reflects the number of chlorines on the ring with the hydroxy substituent. It will be shown later that the quinoxide ion can be formed from the (M - 1)⁻ ion by collision induced dissociation. The observation of one of these ions, however, is not always accompanied by the other

(as in the 4,2', 4'- and 3,4,5,6,4'-isomers) and this may not be the major formation mechanism.

Other ions observed include (M + 35)⁻ adduct ions and various chlorinated phenoxide ions.

CID-MIKES

Two types of CID-MIKES experiments were performed. In the first, mass-analyzed negative ions transmitted by the magnetic sector were collisionally excited and the negative ion fragments analyzed by the electric sector. In the second, the polarity of the electric sector was reversed, and the positive ions produced by charge reversal are sampled. In charge reversal, the structure of the positive ion formed by charge stripping is the same as that of the negative ion precursor, and knowledge of positive ion decompositions can be applied to deduce the structure of the negative ion (18).

The CID-MIKES spectra of selected (M - 1)⁻, (M - 36)⁻, (M - 37)⁻, quinoxide, and chlorophenoxide ions were obtained. Common fragmentations in normal CID-MIKE spectra are summarized in Table 2 and those in the charge-reversed spectra in Table 3.

Table 2. Common fragmentations and ions observed in CID-MIKE spectra.

(M - 1) ⁻	(M - 36) ⁻	(M - 37) ⁻	Quinoxide ions	Phenoxide ions
-HCl or -2HCl phenoxide quinoxide	-H -HCl or 2HCl -H ₂ CO -HCOCl	-HCl -HCO -HCOCl	-CO -HCl -H ₂ COCl -HCOCl	-H -HCO -HCl -HCOCl COCl

Table 3. Common fragmentations observed in charge-reversed CID MIKE spectra.

$(M - 1)^-$	$(M - 36)^-$	$(M - 37)^-$	Quinoxide ions	Phenoxide
-Cl -HCl ₂ CO	-Cl -COCl -HClC ₂ O ₂ -HCl ₂ CO	-Cl -CO -HClC ₂ O ₂ (no losses)	(no losses)	Charge reversal -O -CO -OCl -COCl (no losses)

CID-MIKE spectra of the $(M - 1)^-$ ions from three isomeric tetrachloro- and three isomeric pentachloro-2-phenoxyphenols are shown in Figures 3 and 4, respectively. In each case, the intensities of other fragment peaks should be compared to the intensities of the peaks for loss of HCl, which have been made as nearly equal as practical.

In Figure 2, it can be seen that these trichloro isomers produce different CID-MIKE spectra. Loss of 72 as 2HCl occurs with about equal facility from each isomeric $(M - 1)^-$ ion. The A (3,4,5,4') isomer, produces the appropriate trichloroquinoxide ion. The other two isomers are dichlorosubstituted on the phenol, and form dichloroquinoxide ions. The intensity of this fragment is about 3 times greater for isomer C (3,4,2',4') than for B (4,5,2',4'), and the trichloroquinoxide isomer from A is about 10 times as intense reflecting the increased stability of this latter ion.

The $(M - 1)^-$ ion of isomer A loses 128, 147, and

155 daltons to form fragment ions. These losses are not observed in the spectra of the other two isomers studied. Collisional excitation of the $(M - 1)^-$ ions from both isomers B and C causes fragmentation to form the dichlorophenoxide ion, consistent with the isomer pattern.

In Figure 3, it can be seen that the three pentachloro isomers studied produce different spectra as well. Loss of HCl is common to the spectra of all three isomers, but loss of 2HCl is observed only in two. Isomer D (3,4,5,2',4') produces the trichloroquinoxide ion, as might be expected from previous discussion. The other two isomers are phenoxy di- and tetrachlorophenols and thus do not form this ion. Uncharacteristically, isomer E (4,5,2',4',5') does not form the dichloroquinoxide ion, but only di- and trichlorophenoxide ions. The CID-MIKE spectrum of the $(M - 1)^-$ ion from isomer F (3,4,5,6,4') contains many peaks. Formation of the tetrachloroquinoxide ion is observed, and this peak has an intensity 10-15% that of the

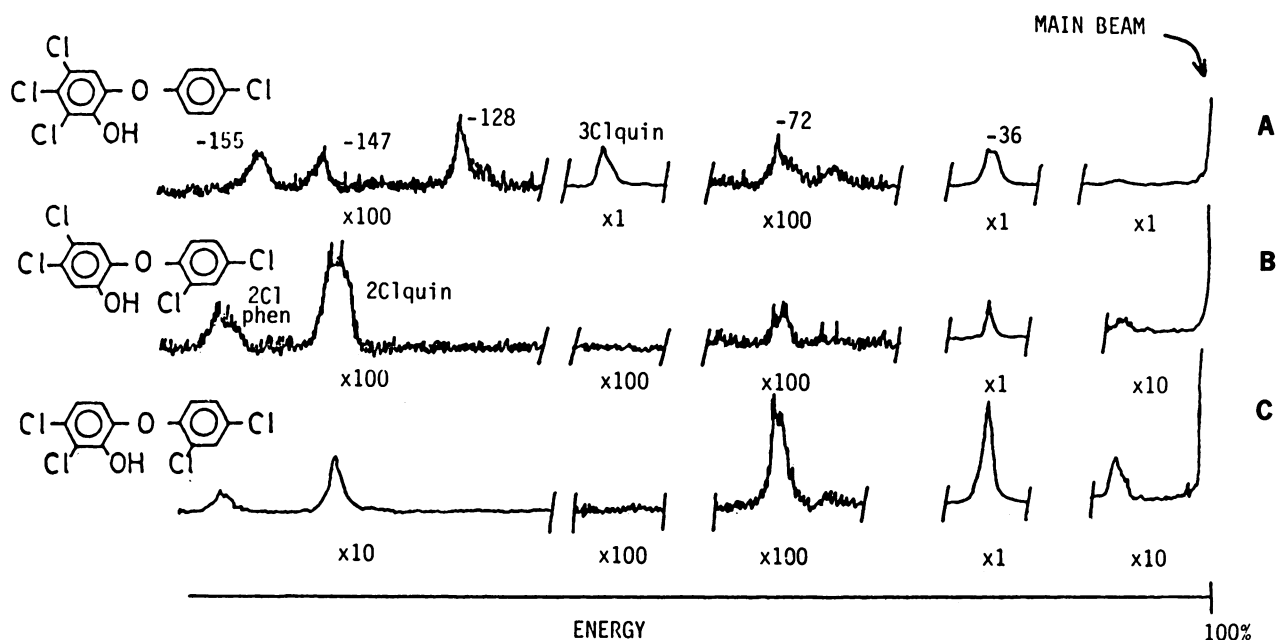


FIGURE 2. CID-MIKE spectra of (A) V, (B) IX, and (C) VII.

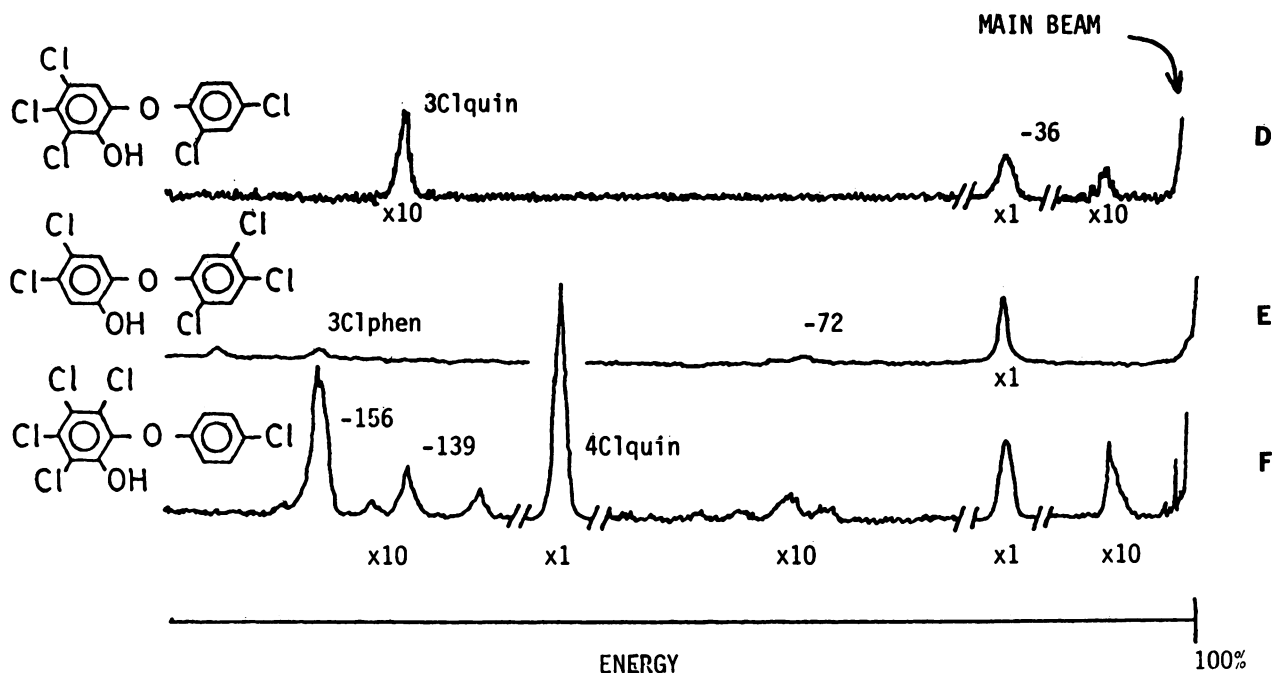


FIGURE 3. CID-MIKE spectra of (D) VI, (E) IX, and (F) X.

main beam. Many other fragments are observed which do not appear in the spectra of the other isomers.

Interestingly, although formation of the tetrachloroquinoxide ion occurs readily from colli-

sionally excited $(M-1)^-$ ions of isomer F, it is not observed in the methane enhanced negative ion mass spectrum of this isomer. If formation of the quinoxide ion requires an $(M-1)^-$ ion intermediate, then the non-collisionally excited

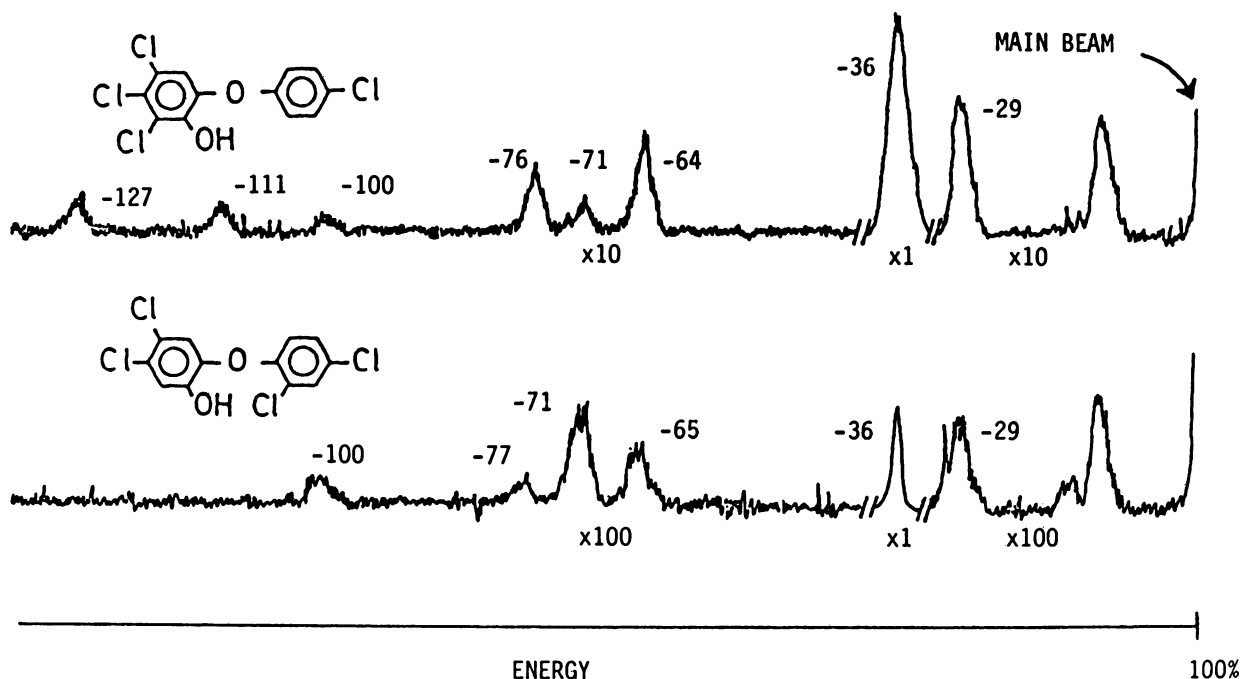


FIGURE 4. CID-MIKE spectra of $(M-36)^-$ ions from two tetrachloro isomers.

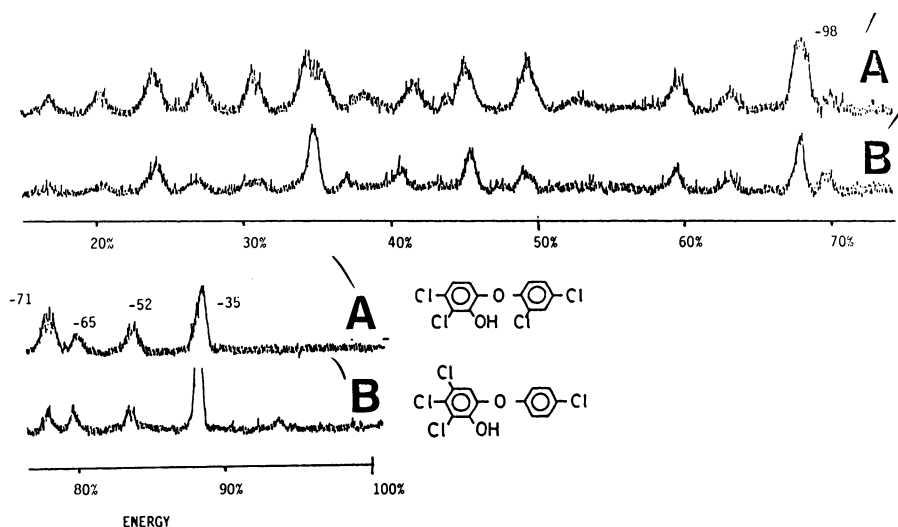
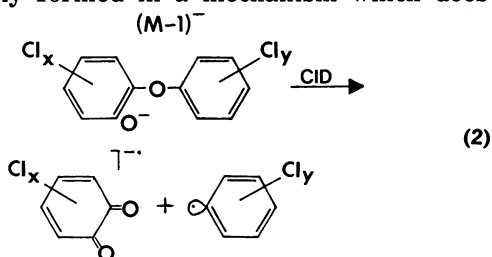


FIGURE 5. Charge-reversed CID-MIKE spectra of two isomeric $(M-1)^-$ ions.

$(M-1)^-$ does not possess enough energy to form the tetrachloroquinoxide. This seems unlikely, since every other 2-phenoxyphenol investigated does undergo this reaction, and the quinoxide ion is probably formed in a mechanism which does



not involve formation of $(M-1)^-$. This hypothesis will be tested by the appropriate linked scan experiments. The mechanism of formation under CID conditions is shown in Eq. (2).

The CID-MIKE spectra of other $(M-36)^-$, $(M-37)^-$, and $(M-72)^-$ ions were obtained. Again, differences in the spectra from isomeric ions could be discerned, as in Figure 4 which shows the spectra of the $(M-36)^-$ ions from two tetrachloro isomers. The common losses are as listed in Table 2. Loss of HCO rather than CO suggests that the hydroxyl hydrogen is still present in the $(M-36)^-$ ion.

Charge-reversed CID-MIKE spectra were obtained for a limited number of ions. Some ions did not produce charge reversal spectra at all, while the spectra of others contained numerous fragments. An example of the latter is shown in Figure 5, which illustrates the charge-reversed CID-MIKE spectra of two isomeric tetrachloro $(M-1)^-$ ions. Although the charge reversed ion does not appear, fragment ions down to about $m/$

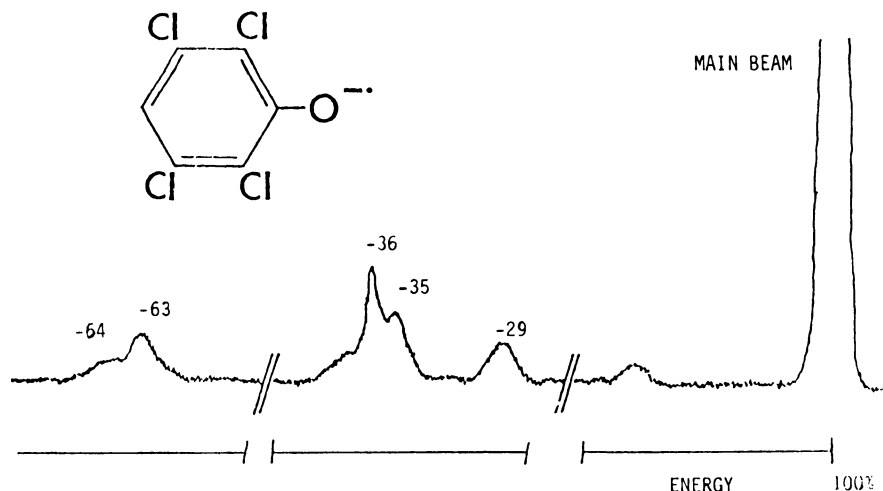


FIGURE 6. Normal CID spectrum of 2,3,5,6-tetrachlorophenoxide ion.

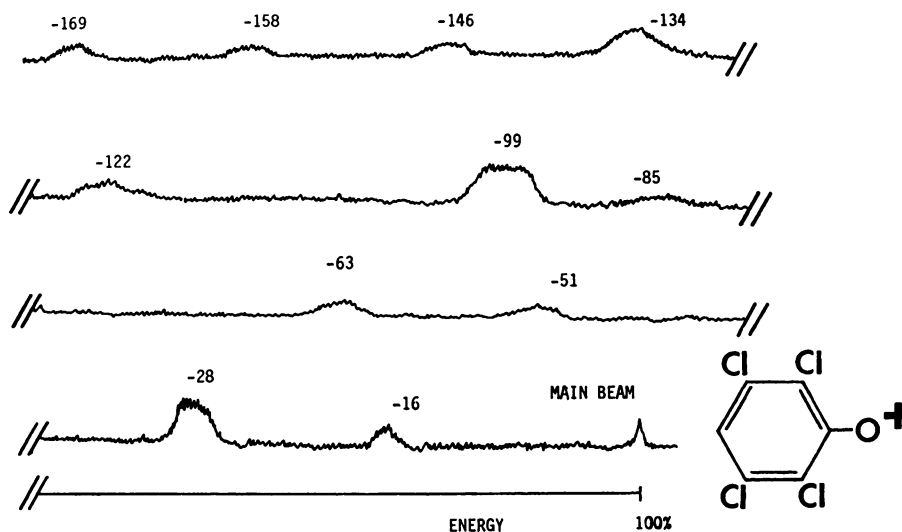


FIGURE 7. Charge-reversed CID spectrum of 2,3,5,6-tetrachlorophenoxide ion.

z 60 are observed. These spectra are very similar, although the analogous nonreversed spectra (shown in Figure 2) are clearly different. The intensities of the fragment from HCl loss and the pattern at about 0.35 E are the only two readily apparent differences.

The CID-MIKES spectra of some quinoxide and phenoxide ions were obtained. Comparison to the spectra of readily available known isomers of these compounds would confirm their proposed identity. The normal and charge-reversed CID spectra of 2,3,5,6-tetrachlorophenoxide ion are shown in Figures 6 and 7, respectively (this ion is found in the spectrum of 3,4,5,2',3',5',6'-heptachloro-2-phenoxyphenol). In Figure 6, the loss of HCO can be observed. Since rearrangements do not occur on collisional excitation, this loss must be the result of two very fast steps. The charge reversed spectrum includes a charge reversed main beam, and numerous losses, including loss of 16 (O), 28 (CO), and 63 (COCl). In view of differentiation of chlorophenol isomers by IKES (19), it is to be expected that the CID-MIKE spectra of these ions can be useful in the determination of the structure of a unknown polychloro-2-phenoxyphenol.

As more isomers of the polychlorinated aromatic hydrocarbons become available, the CID-MIKES studies of these compounds can be expected to become more informative. Not only can the quinoxide or phenoxide ions encountered in the negative ion mass spectrum be compared with known isomers, but comparisons between classes may be possible. As an example, the $(M - 36)^-$ ion from these 2-phenoxyphenol ions may be

formed in the same manner as the thermal or photochemical ring closure loss of HCl to form dioxins. Although dioxins may not always form M^- , charge reversal of the $(M - 36)^-$ from the 2-phenoxyphenol can be compared directly to the CID-MIKE spectrum of the M^+ from the appropriate dioxin. In another case, the $(M - 1)^-$ ion from the 2-phenoxyphenol can be compared to the $(M - 19)^-$ ion from a diphenyl ether.

Conclusions

The methane-enhanced negative ion mass spectra of polychloro-2-phenoxyphenols contain $(M - 1)^-$, $(M - 36)^-$, $(M - 37)^-$, $(M - 72)^-$; quinoxide and phenoxide peaks. The latter two ions provide information about the information about the distribution of chlorines between the two rings.

CID-MIKE spectra of several negative ions from these compounds are sufficiently different to distinguish isomers on a qualitative basis. Charge-reversed CID-MIKE spectra of isomeric species show fewer, but still clear differences. Comparison of the normal and charge-reversed CID-MIKE spectra of quinoxide and phenoxide ions with readily available reference isomers may prove to be the simplest method of isomeric differentiation and identification. Collisional excitation of these small ions produces many fragments, sometimes by multistep processes.

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